

Bis-Porphyrin Racks with Space-Separated Co-Planar Porphyrin Rings

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Abstract: A porphyrin appended norbornenyl building block **8** has been isolated and coupled, using a 1,3-dipolar ACE reaction, to yield *bis*-porphyrin compounds in which the porphyrin moieties are angled upward relative to the norbornane backbone.

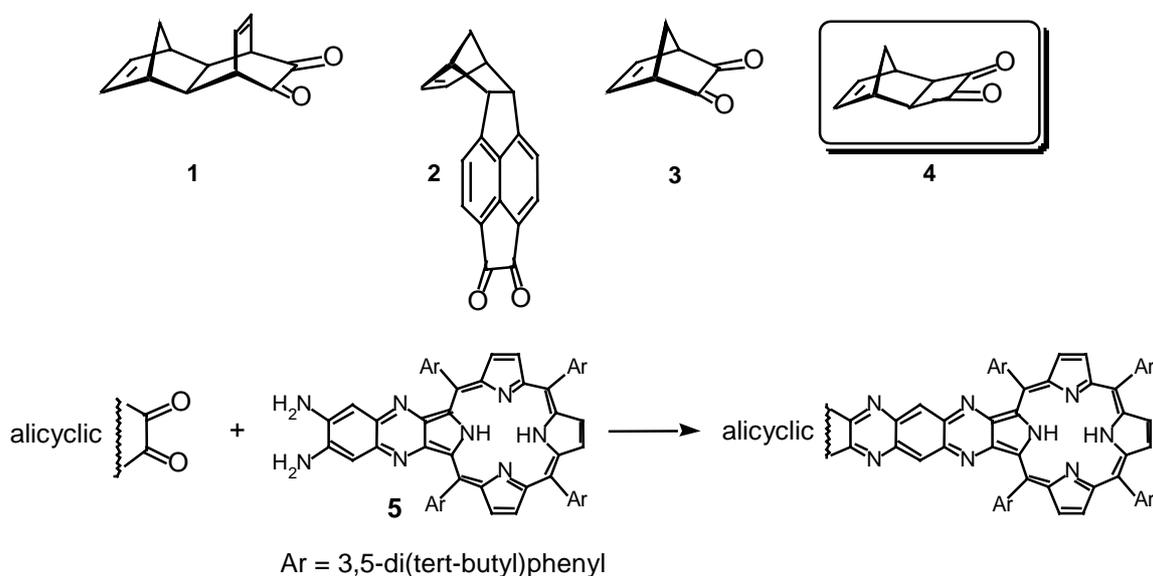
Keywords: porphyrin building block, dipolar coupling, *bis*-porphyrins.

Introduction

Following the elucidation of the strict geometric alignment of chromophores within purple photosynthetic bacteria [1], numerous reports have appeared in the literature regarding approaches to the construction of multiporphyrinic arrays, with a view to mimicking the natural system as a light harvesting machine. Initially, these reports involved the covalent attachment of chromophores [2], however recent efforts in this field have increasingly taken advantage of self-assembly strategies for array construction [3].

The design of new molecular architectures for *bis*-porphyrins and their use in a fundamental study of self-assembly processes has been an active goal of our recent research [4,5]. In earlier papers, we concentrated on the synthesis of V- and U-shaped cavities with the porphyrin macrocycle attached in a fixed geometry by two bonds to the termini of fused carbocyclic frames. Two elements dominate the shape of such systems: a) the topology of the carbocyclic frame and b) the angle of attachment of the

porphyrin ring to the frame. In a preliminary communication on this work [6], we enunciated the use of angled norbornene blocks which carry the porphyrin ring and showed how the topology of the frame could be used to achieve specific geometric outcomes. Implicit in the success of the approach, was the ability to make the angled blocks and to construct the molecular frame with predefined stereochemistry. We found that 1,3-dipolar ACE coupling [7] of cyclobutene epoxides with norbornenes has satisfied the latter requirement and the same reaction protocol is exploited in the present study.



Scheme 1: Various norbornenyl α -diones **1-4** used to produce porphyrin blocks via condensation with diamine **5**.

The norbornene blocks have been functionalised by condensation of norbornene-containing alicyclic α -diones with the Crossley porphyrin diamine **5** [8]. The α -diones **1** [4,6], **2** [6] and **3** [9] used in our earlier work have a geometry in which the α -dione component bears a downward relationship to the norbornene frame that is accentuated following condensation with the porphyrin. Such a geometry is well suited for the construction of U- and V-shaped *bis*-porphyrins as the molecular frame is curved downwards and helps position the porphyrins on the underside of the frame (“southern” systems; substituents on these systems have been designated either “northern” or “southern” depending on their relative orientation to the methano-bridges of the polynorbornane backbone [10]).

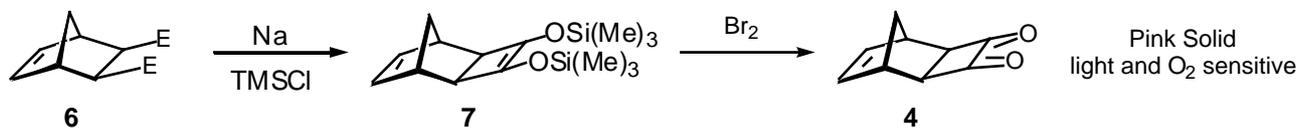
In this paper we discuss the preparation and use of a porphyrin block derived from the upward-directed α -dione **4**. Our new objective has been to use this block to prepare “northern” V-shaped systems by coupling with frames of linear geometry and co-planar *bis*-porphyrins by reaction with curved [n]polynorbornane frames.

Results and Discussion

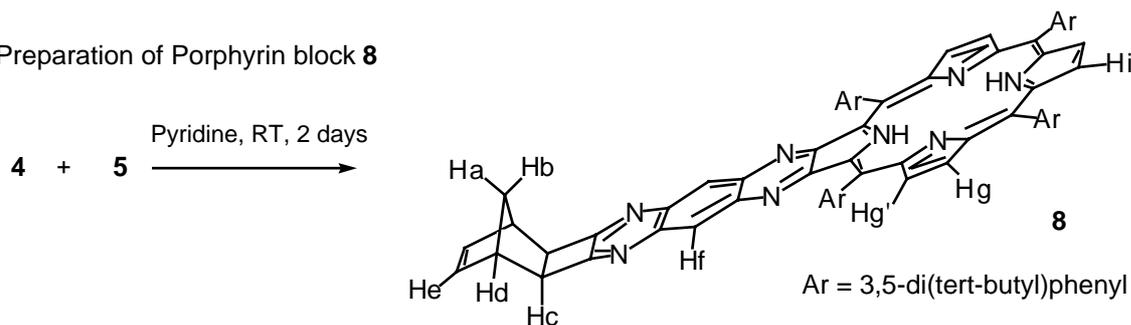
The required α -dione **4** is a known compound and was prepared following the method reported by Martin *et al.* [11] (Scheme 2a). Condensation of **4** with the Crossley diamine **5** [8] produced the porphyrin block **8** (Scheme 2b) that was characterised by spectroscopy and high resolution electrospray

mass spectrometry (HR-ESMS) (found m/z 1307.8294). The $^1\text{H-NMR}$ spectrum of **8** (Figure 1) is typical for porphyrin-appended norbornene blocks with the porphyrin and alicyclic resonances well separated.

a) Synthesis of α -dione **4**



b) Preparation of Porphyrin block **8**



Scheme 2: Synthetic methodologies for isolation of dione **4** and porphyrin block **8**.

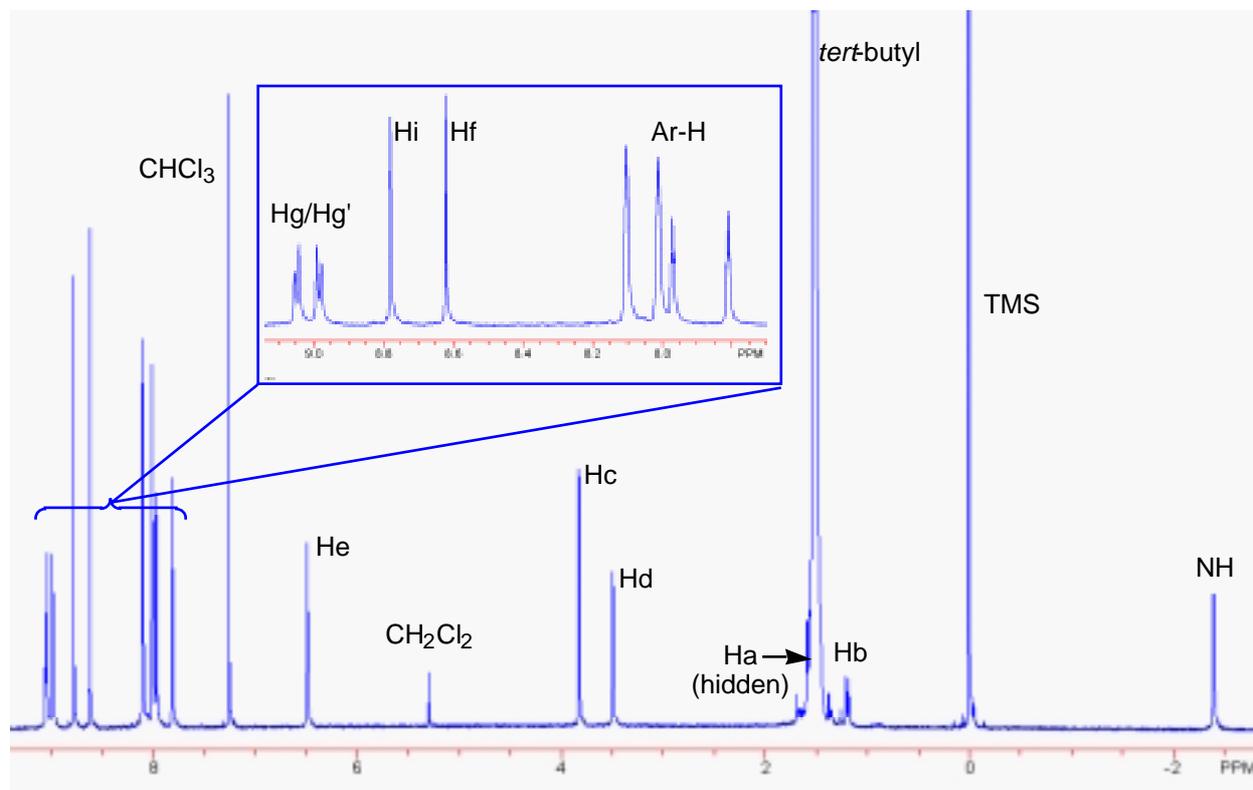


Figure 1: $^1\text{H-NMR}$ spectrum (300 MHz, CDCl_3) of porphyrin block **8**.

The porphyrin resonances, because of the Cs symmetry of **8**, occur as a two doublets for Hg and Hg' (δ 9.04, 8.96) and singlets for Hi (δ 8.78) and the tetrazaanthracene protons Hf (δ 8.62). The aryl protons resonate as two sets (ratio 2:1) reflecting the 3,5-substitution pattern of the aryl ring (δ 8.10 – 7.81). The inner NH protons resonate at δ –2.39 as expected due to the large paramagnetic ring current present in the porphyrin macrocycle. The *tert*-butyl groups present in **8** resonate at δ 1.50 – 1.53 and, in chloroform solution, these resonances overlap with the methano-bridge proton Ha resonance. The presence of the Ha proton resonance was detected by a COSY experiment. The resonance for the vinyl protons (He) occurred as a singlet at δ 6.49 and its presence was used to monitor the progress of the ACE coupling reaction. Typically, protons Hd (allylic) and Hc (benzylic) occur downfield owing to the strong electron-withdrawing effect of the azaheterocycle, accounting for the lower field shift of Hc relative to Hd. The broadening of the latter signal is due to coupling with the methano-bridge protons. Molecular modeling [12] of **8** was carried out at the semi-empirical level of theory (AM1) and revealed the overall shape of the block (Figure 2). The porphyrin macrocyclic ring is angled upward from the norbornene skeleton at an angle of 28° and thereby contrasts with the previously prepared blocks **1** - **3**.

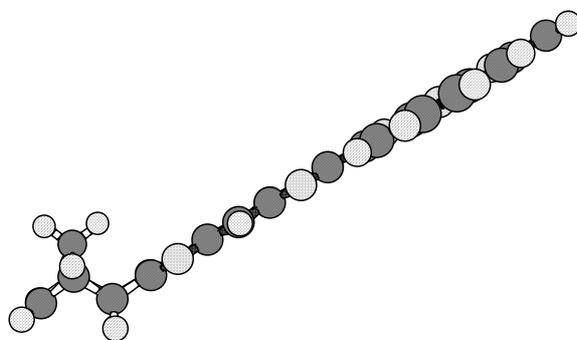
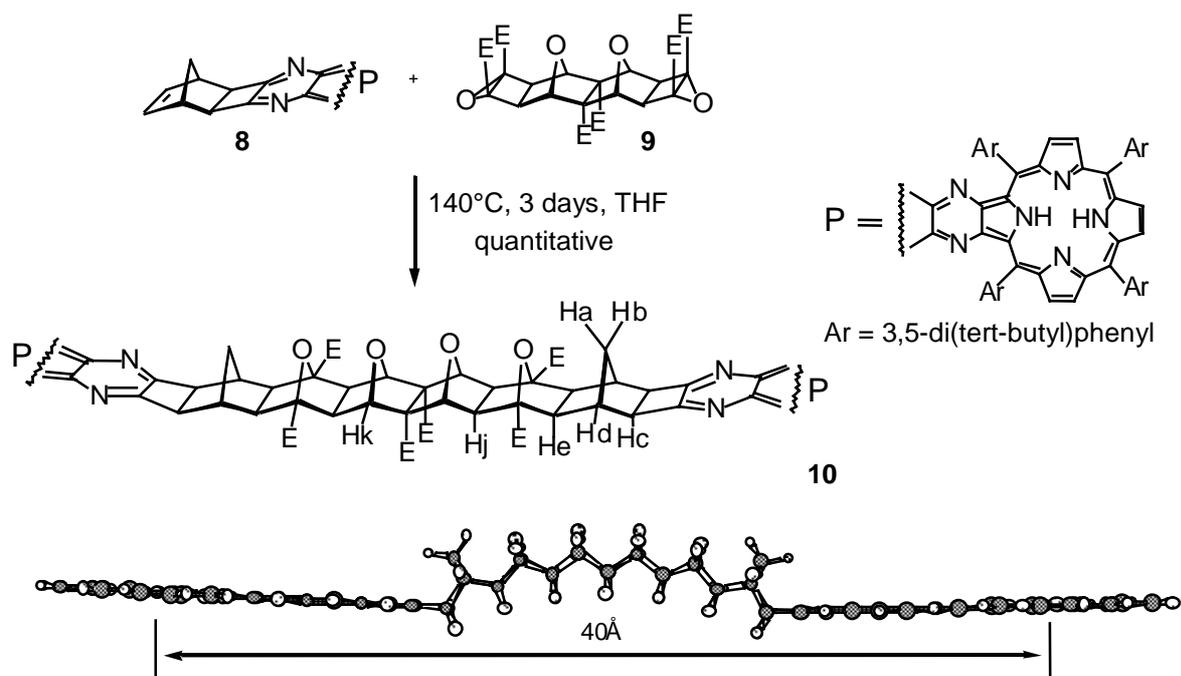


Figure 2: Molecular modeling (AM1) of the porphyrin block **8**.

Several coupling reactions were investigated utilising block **8** to produce *bis*-porphyrin compounds. The coupling reactions were based on the ACE coupling protocol which utilises a 1,3-dipolar cycloaddition strategy in which the dipole is generated *in situ* by ring opening of an epoxide and trapped by the norbornene. In this work, *bis*-epoxide molecules **9**, **11** and **13** were used to yield products of differing geometries due to the different spatial requirements of the *bis*-epoxide spacer backbone.

In the first instance, *bis*-epoxide **9** was heated in a sealed tube with block **8** (Scheme 3) at 140°C for three days to yield the *bis*-porphyrin **10**, which was isolated by chromatographic separation. Once again *bis*-porphyrin **10** was characterised by ^1H NMR spectroscopy (Figure 3) and HR-ESMS with proton resonances being assigned using a combination of 2D COSY and NOESY experiments (in the NOESY spectrum of **10**, in addition to the expected intramolecular signals, several additional cross peaks were observed and which were found to be concentration dependant, however, the ^1H -NMR spectrum of **10** showed no concentration dependant shifts and we are currently investigating this phenomena; a referee is thanked for bringing this to the author's attention).

The proton resonances for the porphyrin moiety are little changed from those observed in **8** except for the alicyclic backbone. The olefinic proton resonance (He) present in block **8** is lost upon coupling, being shifted upfield to δ 2.28 in line with the change in hybridisation.



Scheme 3: Synthesis of *bis*-porphyrin **10** using porphyrin block **8** and *bis*-epoxide **9**.

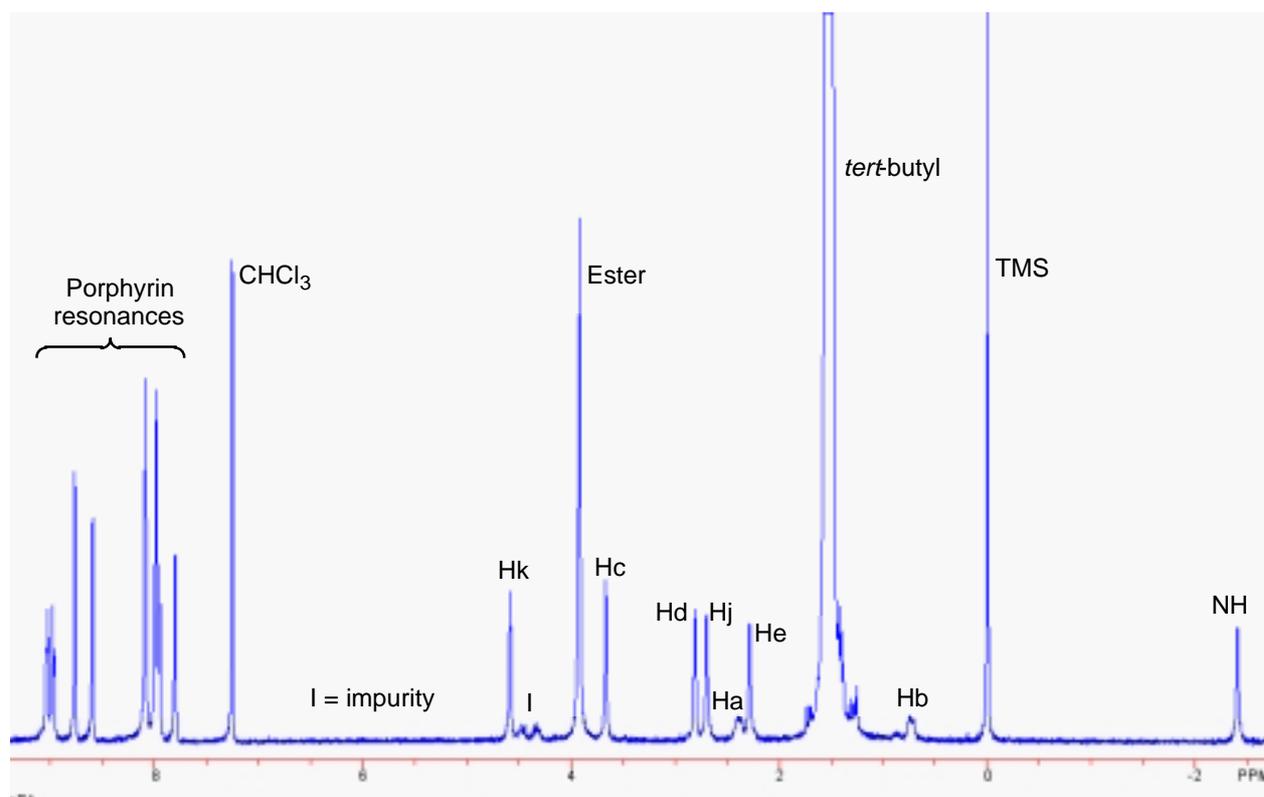
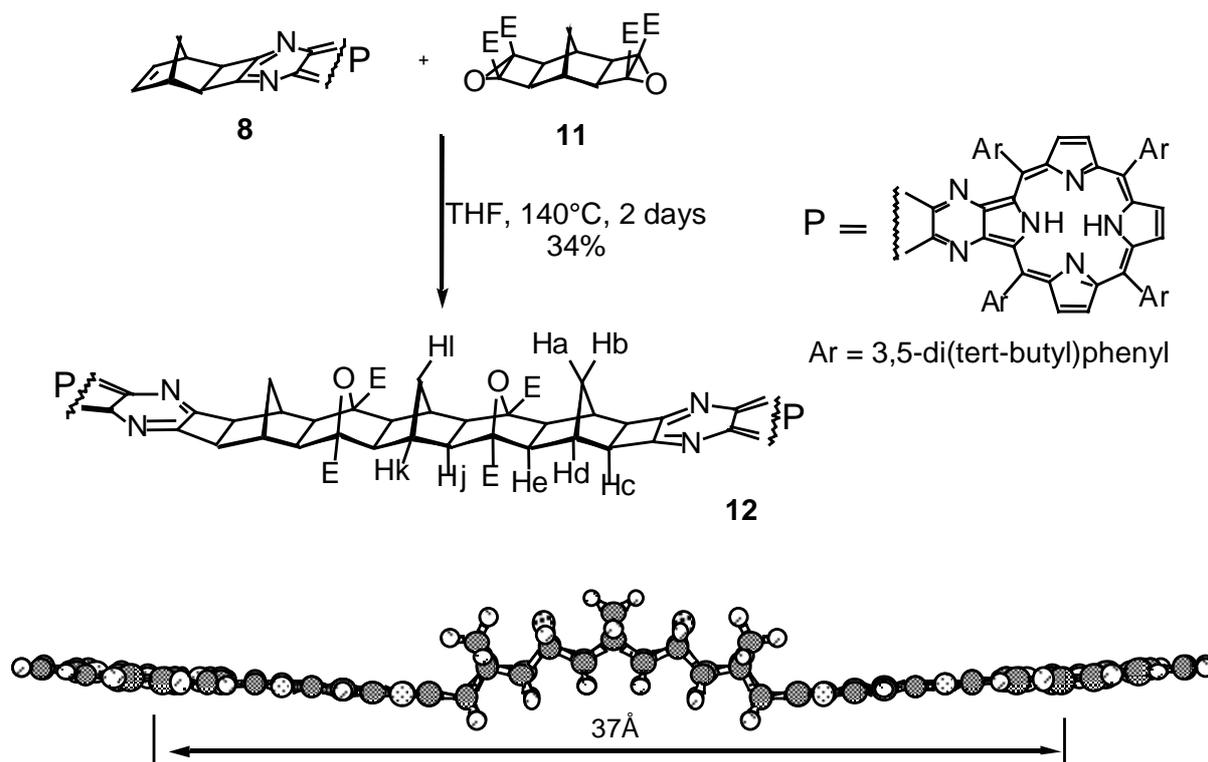


Figure 3: ¹H NMR spectrum (300 MHz, CDCl₃) of *bis*-porphyrin cavity **10**.

Further, the new resonances for methylene protons Ha and Hb are diagnostic (δ 2.40 and 0.72) since Ha is significantly downfield shifted being influenced by the adjacent 7-oxanorbornane system. Such a shift reinforces the linear nature of the coupled product. HR-ESMS yielded a doubly charged molecular ion at the required position (m/z 1605.896). Molecular modeling (AM1) reveals the almost coplanarity of the porphyrin macrocycles within **10**, with each porphyrin plane approximately 2.5° from the horizontal, with an interporphyrin centre-to-centre distance of 40 Å.

Heating of **8** and **11** in a sealed tube (THF, 140°C , 2 days) produced the *bis*-porphyrin **12** in 34% yield after chromatographic purification (Scheme 4). Product identification was confirmed by $^1\text{H-NMR}$ spectroscopy (Figure 4) and HR-ESMS.



Scheme 4: Synthetic scheme outlining the isolation of *bis*-porphyrin **12**.

In a similar manner to **10**, the $^1\text{H-NMR}$ resonances for protons attached to the porphyrin moiety are little affected by the coupling process, yet major changes are observed for the alicyclic backbone proton Ha, Hb, and He resonances. The Ha resonance is influenced by the adjacent 7-oxanorbornane ring and is shifted downfield to δ 2.28, whereas Hb is shifted upfield to δ 0.71. The resonance for He is shifted upfield concomitant with the loss of olefinic character as a result of the coupling reaction. The resonances at δ 2.04 and δ 2.28 represent overlapping signals from several protons and this complication prevents the exact identification of the proton resonances (Figure 4). HR-ESMS again supported the identity of **12** with a doubly charged molecular ion being observed (m/z 1512.889).

Molecular modeling (AM1) of **12** (Scheme 4) again reveals the near coplanarity of the porphyrin macrocycles within **12**, with each porphyrin plane inclined only 4° from the horizontal. The interporphyrin centre-to-centre distance, in this case, was calculated to be 37 Å.

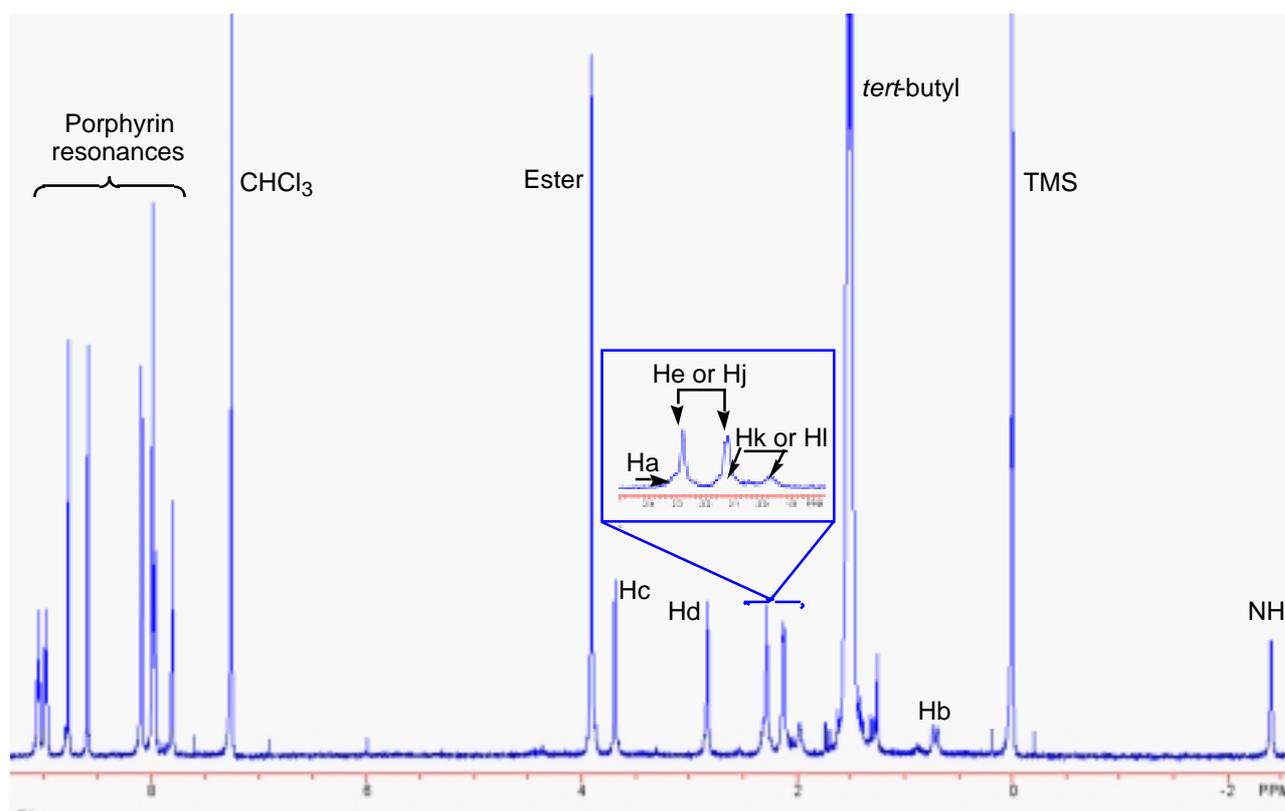
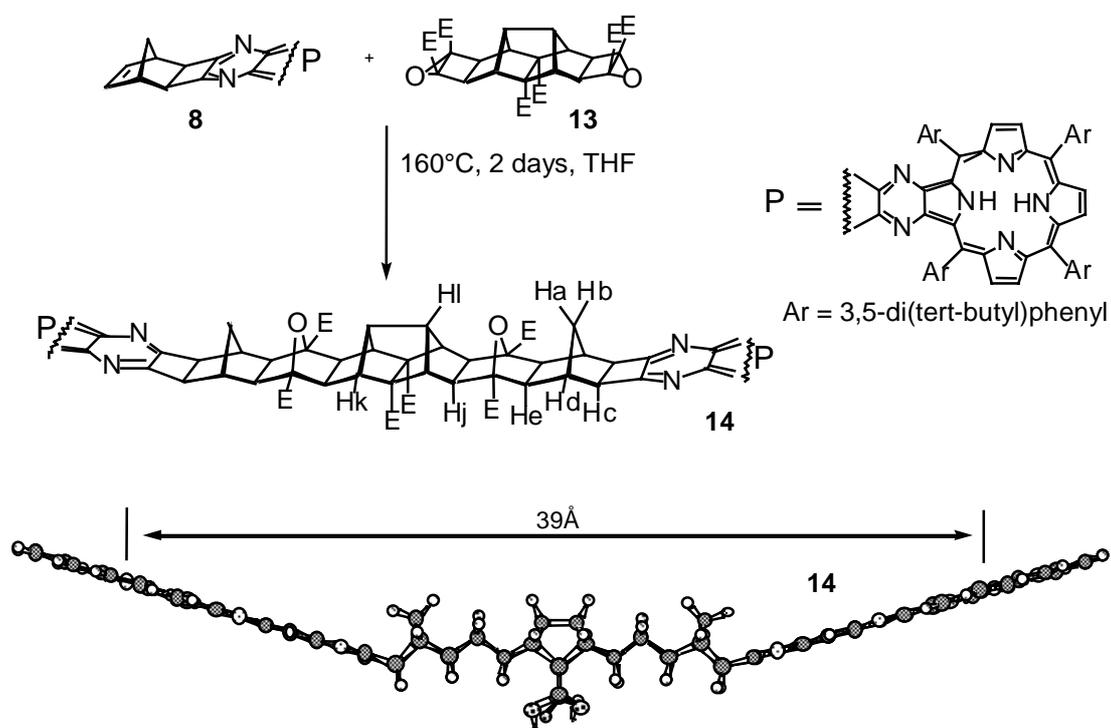


Figure 4: $^1\text{H-NMR}$ spectrum (300 MHz, CDCl_3) of *bis-porphyrin cavity 12*.

Porphyrin block **8** and *bis-epoxide 13* were heated in sealed tube at 160°C for 2 days and yielded **14** in good yield (62%) (Scheme 5). $^1\text{H-NMR}$ resonances were again assigned using a combination of 2D-COSY and NOESY experiments and are shown in Figure 5.



Scheme 5: Synthesis of *bis-porphyrin 14* from porphyrin block **8** and *bis-epoxide 13*.

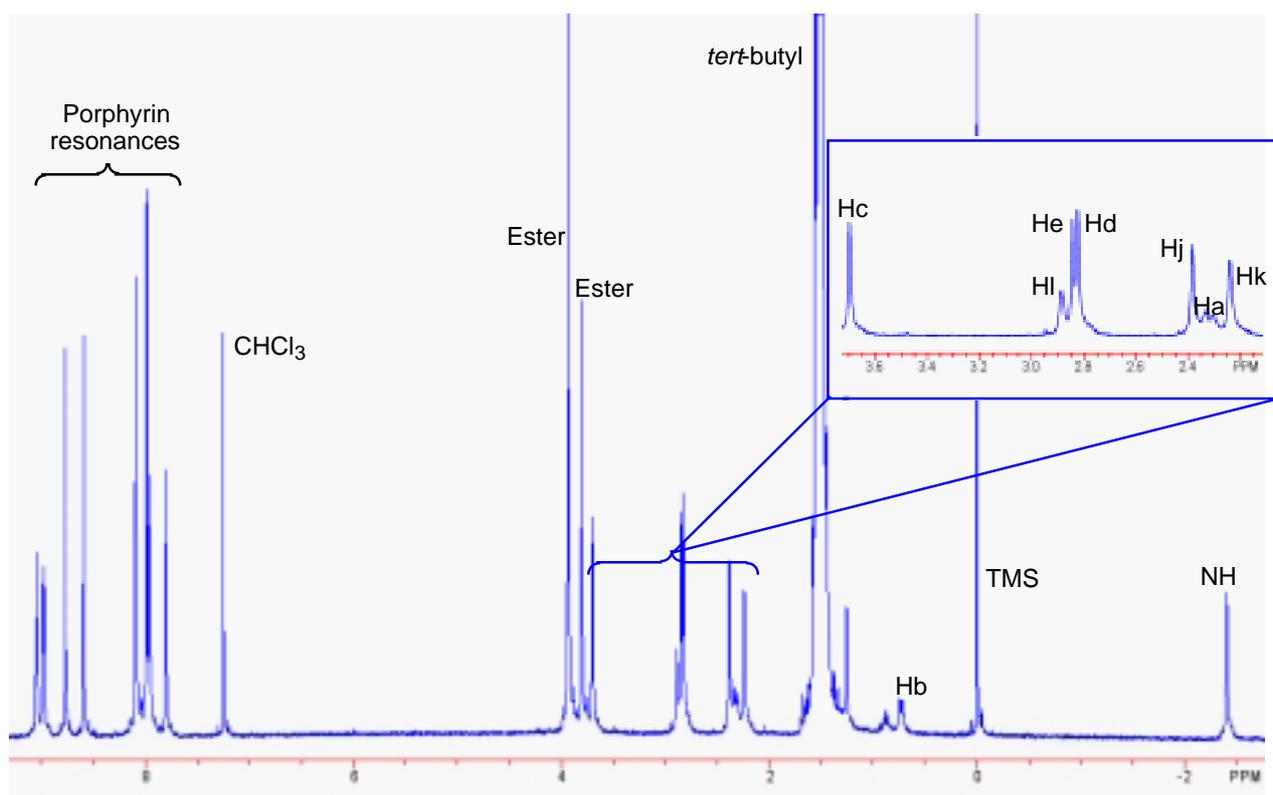


Figure 5: ^1H -NMR spectrum (300 MHz, CDCl_3) of *bis*-porphyrin cavity **14**.

Characteristic ^1H -NMR resonances were again observed for Ha (δ 2.32) and Hb (δ 0.72) and supported the linear geometry for the coupling protocol. The structure of **14** was further supported by the presence of a doubly charged molecular ion observed at m/z 1602.9084 in the HR-ESMS.

Molecular modeling (AM1) of **14** (Scheme 5) revealed that each porphyrin plane is tilted upwards from coplanarity by 17° . Compound **14** represents the first example of a *bis*-porphyrin cavity in which the porphyrin macrocycle is directed upwards relative to the connecting alicyclic backbone. The interporphyrin centre-to-centre separation within **14** was calculated to be 39 Å.

Conclusions

Having successfully isolated **10**, **11** and **12**, current attention is being directed at the examination of the coordination chemistry of their metallated porphyrin derivatives and their ability to coordinate bidentate ligands. In particular, the assembly of the *bis*-porphyrin molecules to create larger supramolecular arrays will be targeted in an attempt to mimic the arrangement of photochromic pigments found in the natural photosynthetic apparatus. The results of these studies will be reported in due course.

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Experimental

General

All solvents were used as supplied with the exception of THF (distilled from Na/Benzophenone) and pyridine (distilled from KOH and stored over molecular sieves). Melting points were determined using GALLENKAMP melting point apparatus and are uncorrected. Thin layer chromatography was performed on pre-coated aluminium sheets on Merck silica gel 60 F₂₅₄ and visualised using visible or UV light (254 and 365nm). Column chromatography was carried out under a positive pressure of air using Merck silica gel (230-400 mesh).

NMR spectra were acquired on either a Bruker AMX300 (300MHz) or Bruker DRX400 (400MHz) using standard Bruker pulse programs. Unless otherwise stated, spectra were recorded at 303K using deuterated CHCl₃ as the solvent with tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are reported as parts per million (ppm) with respect to TMS. Abbreviations used in assigning spectra include: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. Mass spectra (MS) were analysed on Micromass Mass Spectrometer using electrospray (ES) techniques. Bis-epoxides **9**[13], **11**[14], and **13**[15] were kindly supplied by Dr Davor Margetic (CMA).

Porphyrin block 8: Porphyrin diamine **5** (0.45 g, 0.37 mmol) was dissolved in dry, deoxygenated pyridine (4 mL) along with dione **4** (150 mg, 1 mmol) and the solution stirred at ambient temperature under nitrogen in the dark for 2 days. The pyridine was removed under vacuum and the residual solids purified by column chromatography (silica) eluting with dichloromethane (DCM)/petroleum spirit (1:4) to give **8** (0.32 g, 65%). M.p. >350°C. HR-ESMS calculated for C₉₁H₁₀₂N₈ (M+H)⁺ 1307.8305; observed 1307.8294; ¹H-NMR (CDCl₃): δ -2.39 (2H, bs); 1.19 (1H, d, J=9.4 Hz); 1.50 – 1.53 (72H, m); 1.60 (1H, d, J=9.4 Hz, hidden); 3.49 (2H, s); 3.82 (2H, s); 6.49 (2H, s); 7.81 (2H, t, J=1.4 Hz); 7.97 (2H, t, J=1.4 Hz); 8.01 (4H, d, J=1.4 Hz); 8.10 (4H, s); 8.62 (2H, s); 8.78 (2H, s); 8.96 (2H, d, J=4.8 Hz); 9.04 (2H, d, J=4.8 Hz).

Bis-porphyrin adduct 10: Porphyrin block **8** (105 mg, 80 μ mol) was dissolved in THF (1 mL) along with bis-epoxide **9** (23 mg, 38 μ mol) and the solution heated in sealed tube at 140°C for 3 days. The material was taken to dryness and purified by column chromatography (silica) eluting with CHCl₃ which gave **10** as a purple solid (112 mg, quantitative yield based on block consumed). Recrystallised from DCM/MeOH. M.p. >350°C. HR-ESMS calculated for C₂₀₈H₂₃₀N₁₆O₁₆ (M+2H)²⁺ 1605.895; observed 1605.896; ¹H-NMR (CDCl₃): δ -2.40 (4H, bs); 0.72 (2H, m); 1.49 – 1.54 (144H, m); 2.28 (4H, s); 2.40 (2H, m); 2.69 (4H, s); 2.80 (4H, s); 3.66 (4H, s); 3.91 (18H, s); 4.58 (4H, s); 7.80 (4H, t, J=1.6 Hz); 7.95 (4H, s); 7.98 (8H, s); 8.08 (8H, s); 8.59 (4H, s); 8.76 (4H, s); 8.97 (4H, d, J=4.9 Hz); 9.03 (4H, d, J=4.9 Hz).

Bis-porphyrin adduct 12: Porphyrin block **8** (68 mg, 52 μ mol) along with bis-epoxide **11** (10 mg, 25 μ mol) were dissolved in THF (1 mL) and the solution heated in a sealed tube in the dark at 140°C for 2 days. The solution was taken to dryness and the resulting material purified by column chromatography (silica) eluting with DCM/petroleum spirit (1:1) to give recovered **8** (19 mg) followed by CHCl₃/THF

(1%) to yield **12** (19 mg, 34% based on porphyrin consumed). Recrystallised from DCM/MeOH. M.p. >350°C. HR-ESMS calculated for C₂₀₁H₂₂₄N₁₆O₁₄ (M+2H)²⁺ 1512.887; observed 1512.889; ¹H-NMR (CDCl₃): δ -2.40 (4H, bs); 0.71 (2H, d, J=11.7 Hz); 1.49-1.53 (144H, m); 1.97 (2H, bs); 2.04 (6H, bs); 2.28 (5H, m); 2.83 (4H, s); 3.69 (4H, s); 3.91 (12H, s); 7.80 (4H, t, J=1.6 Hz); 7.96 (4H, t, J=1.6 Hz); 7.99 (8H, d, J=1.6 Hz); 8.09 (8H, d, J=1.6 Hz); 8.59 (4H, s); 8.77 (4H, s); 8.97 (4H, d, J=4.9 Hz); 9.05 (4H, d, J=4.9 Hz).

Bis-porphyrin adduct 14: Porphyrin block **8** (90 mg, 69 μmol) along with *bis*-epoxide **13** (15 mg, 25 μmol) were dissolved in THF (500 μL) and the solution heated at 160°C in a sealed tube for 2 days. The solution was taken to dryness and the resultant solid purified by column chromatography (silica) eluting with DCM/petroleum spirit (1:1) to give residual block **8** (17 mg) followed by CHCl₃/EtOAc (5%) to yield **14** (69 mg, 62%). Recrystallised from DCM/MeOH. M.p. >350°C. HR-ESMS calculated for C₂₁₀H₂₃₂N₁₆O₁₄ (M+2H)²⁺ 1602.9078; observed 1602.9084; ¹H-NMR (CDCl₃): δ -2.40 (4H, bs); 0.72 (2H, d, J=10.7 Hz); 1.49-1.55 (144H, m); 2.23 (4H, s); 2.31 (2H, d, J=10.7 Hz); 2.38 (4H, s); 2.82 (4H, s); 2.84 (4H, s); 2.88 (2H, s); 3.69 (4H, s); 3.80 (6H, s); 3.93 (12H, s); 7.80 (4H, s); 7.96 (4H, s); 7.99 (8H, s); 8.09 (8H, s); 8.59 (4H, s); 8.77 (4H, s); 8.97 (4H, d, J=4.7 Hz); 9.04 (4H, d, J=4.7 Hz).

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Sample availability: Available from the author.